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Anion-Specific Aggregation Induced Phosphorescence Emission (AIPE) in an Ionic Iridium Complex in Aqueous Media†

Guangfu Li,‡[a] Wei Guan, ‡[a] Shuang Du,[b] Dongxia Zhu,[a]* Guogang Shan,[a] Xiaojuan Zhu,[b] Likai Yan,[a] Zhongmin Su,[a]* Martin R. Bryce[c]* and Andrew P. Monkman[d]

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Efficient Aggregation Induced Phosphorescence Emission (AIPE) of an ionic Ir(III) complex occurs when the counterion (PF_6^-) is exchanged specifically by ClO_4^- in aqueous media. As a result, a rapid, highly selective "turn-on" phosphorescent response to ClO_4^- is observed in aqueous media. These studies pave the way for a new efficient phosphorescence-based detection strategy for anions.

Ionic transition metal complexes (iTMCs), notably those of Ir(III) and Pt(III), are of considerable interest[1] due to their high photoluminescence quantum yields (PLQYs) at room temperature, physicochemical stability and long (several microseconds) PL lifetimes (τ),[2] leading to their applications as light-emitting electrochemical cells (LECs), biological labels, chemosensors for inorganic ions, data recording and security protection devices.[3] The photophysical properties of iTMCs are attributed primarily to strong spin–orbit coupling within the cations. However, the counter anions can also have a profound effect on the photophysical properties[3b] and LECs performance.[4] Therefore, it is important to investigate further the role of counterions in the applications of iTMCs.

The selective detection of certain anions is of vital significance.[5] For example, perchlorate is a major contaminant resulting from the industrial and commercial applications of perchlorate salts which are highly soluble and stable in water. Due to their similar ionic radii, perchlorate can inhibit iodide intake in the thyroid gland, thereby impacting human health.[6] Therefore, the determination of trace levels of ClO_4^- in environmental and biological samples is very important. The detection of anions by fluorescence techniques[7] has limitations due to: 1) fluorescence "turn-off" rather than "turn-on" is usually observed and therefore the sensitivity is limited due to competing fluorescence quenching by heavy metal ions;[8] 2) many systems work in organic solvents, but when water is added, the response becomes difficult to detect.

Aggregation-induced emission (AIE) fluorophores, which show weak emission when dispersed, but emit efficiently when aggregated or in the solid state[9] are attracting great attention,[10] and have been applied for the fluorescent turn-on detection of various ions.[11] However, the highly selective turn-on detection of anions in aqueous media by AIE is rare.[6b,12] For anion detection in vivo, the output signal of AIE-active fluorophores always suffers from the interference of short-lifetime background fluorescence and scattered light.[13] We considered that aggregation-induced phosphorescent emission (AIPE) using iTMCs may be an alternative, unexplored strategy for the turn-on detection of anions due to the long lifetime of phosphorescent emission. Moreover, compared with netural complexes, iTMCs could show highly selective recognition of anions through the interactions between the cation and anion moieties.

Herein, we demonstrate that the new ionic dinuclear Ir(III) Schiff base complex 1•2PF_6 (Fig. 1a) shows a highly selective response for the turn-on phosphorescent detection of ClO_4^- in aqueous media and HeLa cells. To the best of our knowledge, this is the first report of an iTMC used in phosphorescent turn-on detection of an anion by AIPE.

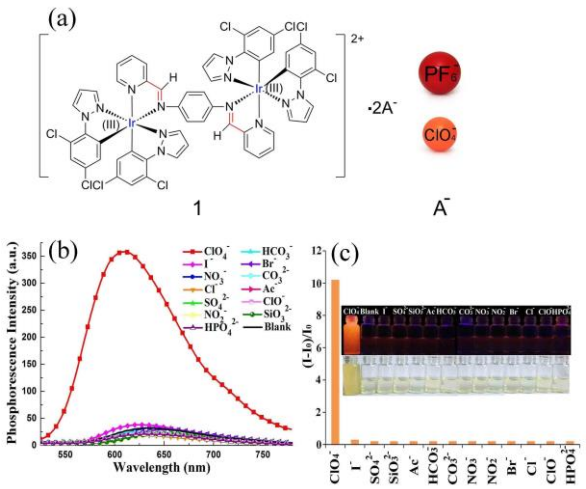

Fig. 1 (a) Chemical structure of complexes **1**•2PF_6 and **1**•2ClO_4; (b) Phosphorescence spectra of **1**•2PF_6 (10 μM) in the presence of different anions (15 equiv.) in 10 mM HEPES buffer (CH_3CN:H_2O, 1:4, v/v); (c) The corresponding phosphorescence variations of **1**•2PF_6. Insert: photographs of **1**•2PF_6 with different anions (15 equiv.) under UV lamp irradiation (top) and sunlight (bottom).

Complex **1**•2PF_6 is AIPE-active[14] (Fig. S1 and Table S1). The faint emission in pure acetonitrile solution can be ascribed to structural distortions in the complex's T_1 geometry compared to the S_0 geometry (Table S2). These distortions induce excited-state relaxations which suppress radiative decay.[15] However, in the solid state, intermolecular π–π or C–H…π interactions between the phenyl rings can restrict intramolecular relaxation favouring a more planar geometry which activates the AIPE (Fig. S2).

Anion recognition was studied by monitoring the phosphorescence of **1**•2PF_6 (10 μM) in HEPES buffer (10 mM in CH_3CN/H_2O, 1/4, v/v, pH 7.4) upon addition of 15 equiv. of ClO_4^-, I^-, Br^-, Cl^-, HCO_3^-, Ac^-, NO_2^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, SiO_3^{2-}, ClO^- or HPO_4^{2-} anions and shaking the sample by hand for a few seconds (Fig. 1b and 1c). A 1:4 ratio of CH_3CN:H_2O was optimum for solubilizing the complex and observing AIPE. For ClO_4^-, phosphorescent turn-on was observed with a long decay time (0.24 μs), λ_{max} blue-shifted by 25 nm and the PLQY increased to 0.12, which is 430 times higher than that of the blank (0.29×10^{-3}) (Fig. S3). The blue shift may be due to a counterion effect, as observed previously in anion exchange experiments.[3b] Remarkably, the addition of all other anions caused no significant change in the emission. The variation of photophysical data for ClO_4^- is accompanied by aggregation which enables the detection of anions readily by the naked eye in daylight (Fig. 1c).

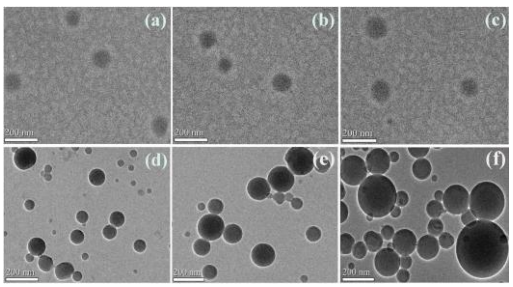

Fig. 2 TEM images of nanoparticles obtained from anion titration experiments of **1**•2PF_6 (10 μM) with (a) blank; (b) 10 equiv. HPO_4^{2-}; (c) 10 equiv. I^-; (d) 3 equiv. ClO_4^-; (e) 5 equiv. ClO_4^-; (f) 10 equiv. ClO_4^- in 10 mM HEPES buffer (CH_3CN:H_2O, 1:4, v/v).

The formation of nano-aggregates was established by transmission electron microscopy (TEM) and dynamic light scattering (DLS) experiments. TEM reveals the nano-aggregates in the titration of **1**•2PF_6 (10 μM) with ClO_4^-; their average sizes increased with the incremental addition of ClO_4^- (Fig. 2a, 2d, 2e and 2f). However, the average sizes are unperturbed in the presence of HPO_4^{2-} and I^- (Fig. 2b and 2c). DLS measurements revealed an enhanced light-scattering intensity on addition of 15 equiv. of $NaClO_4$ in HEPES buffer to **1**•2PF_6 (10 μM), with an average particle size of 405 nm (Fig. S13). However, there was no significant change when 15 equiv. of NO_3^- or Br^- ions were added to **1**•2PF_6 and the average particle size decreased to 120 nm. These results indicate that aggregation was specifically controlled by perchlorate salt. We propose that nano-aggregate formation is a critical factor in enhancing the emission.

Titration experiments with the addition of ClO_4^- to **1**•2PF_6 in HEPES buffer showed no further increase in phosphorescence intensity beyond 15 equiv. of ClO_4^- (Fig. S4a). There is a good linear relationship between the emission intensity of **1**•2PF_6 and ClO_4^- concentration (R^2 = 0.96, 2-120 μM), suitable for quantitative detection of ClO_4^-. The Hill coefficient *n* is 0.67 indicating that the binding between **1**•2PF_6 and ClO_4^- is 1:2 stoichiometry (Fig. S5) which is consistent with the theoretical ion ratio in the complexes. The UV titration experiments showed that the absorption bands of **1**•2PF_6 at ca. 330 nm decreased upon addition of ClO_4^- and the tail above 500 nm increased gradually (Fig. S4b). This is ascribed to the light scattering effect of the formed nano-aggregates which is consistent with the TEM and DLS results.[16]

Competition experiments for the system composed of **1**•2PF_6 and 15 equiv. of ClO_4^- showed that the emission intensity is unperturbed in the presence of 15 equiv. of a range of other anions (Fig. S6). Moreover, the titration of **1**•2PF_6 with ClO_4^- in the presence of potential competing cations, such as Na^+, Li^+, Mn^{2+} and Hg^{2+}, showed only a slight effect on the emission (Fig. S8). These results demonstrate that **1**•2PF_6 has a strong affinity and selectivity for ClO_4^-. The phosphorescence intensity of **1**•2PF_6 containing 15 equiv. of ClO_4^- is also unaffected over the pH range 1-14 (Fig. S9). The lowest detection limit of ClO_4^-, as determined from a plot of normalized phosphorescence intensity as a function of the concentration of added ClO_4^-, is as low as 0.05 ppm (Fig. S10). Therefore, this complex shows highly selective and sensitive phosphorescent turn-on detection of ClO_4^- in the presence of different cations, anions and pH values which is sufficient to detect ClO_4^- pollution in Eco-water.

To understand the origin of the selectivity of **1**•2PF_6 towards ClO_4^-, ^{19}F NMR experiments were performed. **1**•2PF_6 was added to an internal standard of 1-iodo-3-(trifluoromethyl)benzene in the molar ratio (standard: **1**•2PF_6 = 16:1). Figure S14a shows that the integral area ratio between the standard and **1**•2PF_6 is 4:1. However, for a solution of the light yellow precipitate from a ClO_4^- titration experiment, the integral area ratio (standard: complex) is 20:1 (Fig. S14b) showing that partial anion exchange has occurred from PF_6^- to ClO_4^-.

MALDI-TOF negative-ion mass spectrometry further verified which anions exchange the PF_6^- of **1**•2PF_6. After adding 15 equiv. of ClO_4^-, Br^- or NO_3^- to **1**•2PF_6 (in CH_3CN:H_2O, 1:4, v/v), the mass spectra of the filtrates were recorded (Fig. S14c, S14d and S14e). The peaks at *m/z* 98.7 and 144.7 correspond to ClO_4^- and PF_6^-, respectively. In contrast, only the peak at *m/z* 144.7 appeared with added Br^- and NO_3^-. These results are in agreement with the ^{19}F NMR studies and indicate that only ClO_4^- readily exchanges PF_6^-.

The specificity for ClO_4^- is supported by DFT calculations. The binding energy for complex **1** with ClO_4^-, ClO^-, Br^-, Cl^-, HCO_3^-, Ac^-, NO_2^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, SiO_3^{2-} or HPO_4^{2-} anions in the presence of counter cations, is listed in Table S3. The formation of the perchlorate adduct is exothermic by −10.1 kcal mol^{-1} in the gas phase and −8.6 kcal mol^{-1} in acetonitrile solution (Fig. 3 and entry 1 in Table S3) whereas all the other reactions are endothermic (entries 2-10 in Table S3). Therefore, the highly

selective detection of ClO_4^- is consistent with thermodynamics data.

To investigate the mechanism of the phosphorescent turn-on response to perchlorate, *trans*-*cis* isomerization for **1**•2PF_6 and **1**•2ClO_4 was evaluated by DFT calculations (Fig. 3).

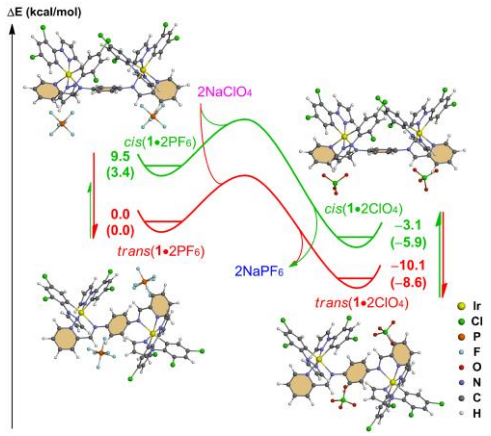

Fig. 3 Optimized structures and relative energies (in kcal mol^{-1}) of *cis* and *trans* isomers of **1**•2PF_6 and **1**•2ClO_4. In parentheses, CPCM(acetonitrile)/M06/[6-31G*/LANL2DZ(Ir)] data are shown.

The *trans*-conformation is more stable than the *cis* in both cases; however, the energy difference between the two conformations decreases upon exchanging PF_6^- for ClO_4^- in both solution and the gas phase. This implies that isomerization of **1**•2ClO_4 can occur more readily and the ratio of *cis*-conformation will be larger for **1**•2ClO_4 than for **1**•2PF_6. This is verified by the following experimental observations. Firstly, single crystal X-ray structures of **1**•2ClO_4 reveal two conformations, namely *trans*-**1**•2ClO_4 and *cis*-**1**•2ClO_4. However, for **1**•2PF_6 only the *trans*-conformation was obtained, because the large energy difference between *cis*- and *trans*-conformations favors the more stable isomer.[17] Secondly, the ^{1}H NMR data for **1**•2PF_6 and **1**•2ClO_4 (Fig. S16, S17 and S18) show that both complexes have two conformations in the solid state. The ratio of *cis*:*trans* is larger in **1**•2ClO_4 than in **1**•2PF_6 and the two conformations of **1**•2ClO_4 have been readily isolated (Fig. S19 and S20) due to the high solubility of *trans*-**1**•2ClO_4 in hot dichloromethane compared to *cis*-**1**•2ClO_4. This is a rare example where the *cis*- and *trans*-conformations of a dinuclear metal complex have been separated.[18] ^{1}H NMR titration experiments of **1**•2PF_6 with ClO_4^- were carried out in CH_3CN:H_2O (1:4 v/v, pH 7.4) (Fig. S21). Compared with **1**•2PF_6 (Fig. S16), the ratio of *cis*-conformation increases upon the addition of ClO_4^-.

Thirdly, the X-ray crystal structures of **1**•2PF_6 and **1**•2ClO_4 (Fig. 4) show that the bridging ligand of *cis*-**1**•2ClO_4 has a smaller distortion (46°, 55°) and a more planar geometry than both the *trans*-**1**•2ClO_4 and *trans*-**1**•2PF_6 conformations. We conclude that this change of geometry affects the solubility of the complexes, and aggregation (as observed in the TEM studies, Fig. 2) is induced by the increased ratio of the *cis*-conformation during the titration process.

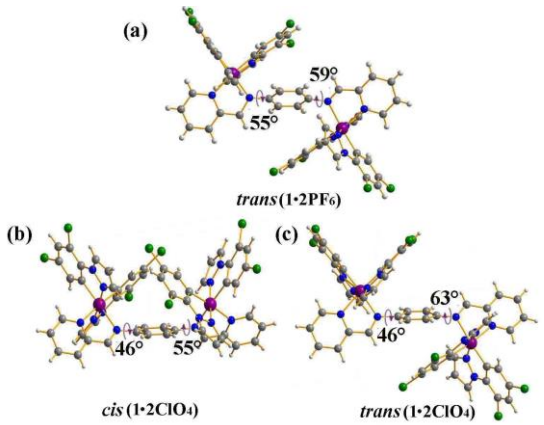

Fig. 4 The dication in the X-ray molecular structures of (a) *trans*-**1**•2PF_6, (b) *cis*-**1**•2ClO_4 and (c) *trans*-**1**•2ClO_4 in the crystal. The anions and solvent molecules are omitted for clarity.

To further understand the large enhancement of the emission when nano-aggregates are formed by addition of ClO_4^-, PLQYs and lifetimes of the complexes in the solid state were determined (Table S1). *Cis*-**1**•2ClO_4 has a significantly higher PLQY (31%) than both **1**•2PF_6 (17%) and *trans*-**1**•2ClO_4 (13%). Moreover, *cis*-**1**•2ClO_4 has a higher radiative rate than both **1**•2PF_6 and *trans*-**1**•2ClO_4. A distorted geometry (*trans*-conformation) would favour non-radiative processes, whereas the more planar geometry (*cis*-**1**•2ClO_4) would increase radiative processes, as observed previously.[15,19] Furthermore, the photoluminescence (PL) spectra of *cis*-**1**•2ClO_4 and *trans*-**1**•2ClO_4 in CH_3CN–H_2O mixtures with various water contents were investigated (Fig. S11). *Trans*-**1**•2ClO_4 in pure CH_3CN exhibits faint emission which is only slightly enhanced when the water content increased to 90% v/v. However, the PL intensity of *cis*-**1**•2ClO_4 is significantly enhanced when the water content exceeds 80% v/v, and is about 20-fold greater than for the *trans*-**1**•2ClO_4 system. The result confirms that *cis*-**1**•2ClO_4 has a significant AIE effect. Therefore, the large ratio of the *cis*-conformation with enhanced AIE performance is responsible for turning on the phosphorescence in ClO_4^- titration experiments.

All the data obtained point to the anion-exchange induced AIPE being responsible for the large phosphorescence enhancement in the detection of ClO_4^-, consistent with the crystal structure analysis, ^{1}H NMR titration experiments and DFT calculations. We explain this anion recognition mechanism as: 1) PF_6^- is exchanged specifically by ClO_4^-, and **1**•2PF_6 has high selectivity for ClO_4^-, 2) ClO_4^- induces *trans* to *cis* conformational isomerisation, 3) turn-on phosphorescence anion recognition is realized by the larger ratio of *cis*-**1**•2ClO_4 inducing AIPE.

We have further studied the potential anion recognition properties of **1**•2PF_6 in vivo. Traditional iTMCs are often very sensitive to oxygen in solutions and exhibit significantly shortened lifetimes which limit their practical applications. However, AIPE-active iTMCs can avoid interference from oxygen due to the complexes being encapsulated within the nano-particles formed in suspension, which can protect them from

oxygen.[13] Therefore, AIPE-active iTMCs may be an ideal choice as an in vivo probe. Preliminary results on **1**•2PF_6 as a probe for ClO_4^- in living cells have been obtained. HeLa cells (from liver cancer cells) were incubated with ClO_4^- (30, 90, 200 μM, respectively) for 15 min at 37 °C and then supplemented with **1**•2PF_6 (10 μM) at 37 °C for another 30 min, and washed with phosphate buffer saline (PBS) to remove the remaining complex. Confocal laser scanning microscopy revealed a clearly enhanced red phosphorescence in the cell membrane with an increased amount of ClO_4^- compared to the data obtained without added ClO_4^- (Fig. 5). Complex **1**•2PF_6 is, therefore, a potential probe for phosphorescence imaging of ClO_4^- in living cells. These are initial proof-of-concept results.

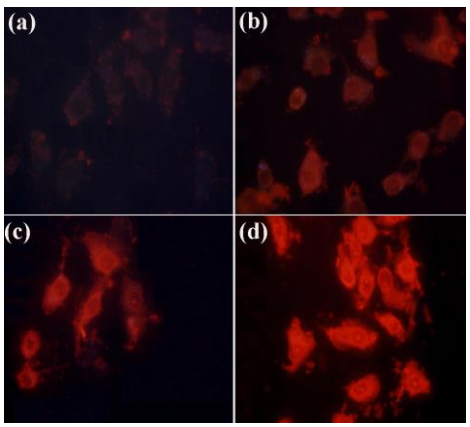

Fig. 5 Phosphorescence images of the HeLa cells cultured in the presence of complex **1**•2PF_6 (10 μM) at 37 °C for 30 min (a); Phosphorescence images of the HeLa cells cultured in the presence of $NaClO_4 \cdot H_2O$ (30, 90, 200 μM, respectively (b), (c), (d)) for 15 min, followed by addition of complex **1**•2PF_6 (10 μM) at 37 °C for another 30 min.

In summary, a new dinuclear ionic iridium complex **1**•2PF_6 shows a rapid, highly selective phosphorescent turn-on response to perchlorate in aqueous media by aggregation induced emission. The structural versatility of iTMCs will enable the scope of this new "anion-exchange induced AIPE" process to be explored in the selective phosphorescence-based detection of anions, for which it may be a general strategy. Dinuclear complexes may be beneficial as the bridging ligand confers additional conformational flexibility compared to mononuclear analogues.

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Notes and references

[a]*Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Renmin Road 5268, Changchun 130024 P.R. China;*
E-mail:zhudx047@nenu.edu.cn; zmsu@nenu.edu.cn
[b]*Key Laboratory of Molecular Epigenetics of the Ministry of Education, Institute of Cytology and Genetics, Northeast Normal University, Renmin Street No. 5268, Changchun, 130024, P. R. China;*
E-mail: zhuxj720@nenu.edu.cn
[c]*Department of Chemistry, Durham University, Durham, DH1 3LE, UK;*
E-mail: m.r.bryce@durham.ac.uk
[d]*Department of Physics, Durham University, Durham DH1 3LE, UK;*
E-mail: a.p.monkman@durham.ac.uk

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‡ These authors contributed equally to the preparation of this work.

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